

Organic Chemistry 2018- Reusable Mesoporous Solid-Based Pd Catalysts for C-C Bond Formation in Water

Ying Wan

Shanghai Normal University, P R China

Environmentally benign, operationally simple, and robust reactions, particularly those employing reusable solid catalysts and water as a solvent, are of significant interest to the chemical industry. Here, heterogeneous palladium catalysts supported on ordered mesoporous carbonaceous nanocomposites including carbon-silica, CoO-C and quaternary ammonium phase transfer agent modified mesoporous carbonaceous resins, were applied to the water-mediated C-C bonds formation. The mesoporous Pd/CoO-C catalyst showed a high yield of biphenyl (49%) in the water-mediated Suzuki coupling reaction of chlorobenzene and phenylboronic acid. Product yields in the reaction of aryl chlorides containing electron-withdrawing groups attached to their benzene ring can reach approximately 90%. Very small Pd clusters consisting of approximately 3 atoms and Pd-O bonds formed on the interface between CoO and Pd nanoparticles. The unsaturated coordinative Pd may be responsible for the activation of chlorobenzene in the absence of any additives or ligands. A nitrogen-containing functional group modified and ordered mesoporous resin material was also used to support a reusable solid Pd catalyst. The grafted quaternary N coordination with highly dispersed Pd NPs creates an electronically rich environment for surface atoms and causes a distinct enhancement in the stabilization and accessibility of these particles to organic substances in aqueous solution. The mesoporous Pd catalysts are active in the C-2 arylation of N-methylindole when water is used as the solvent without any other additive or the exclusion of air. The catalysis likely occurs on the Pd surface rather than in solution. thiol-functionalized mesoporous silica, which can trap soluble Pd species, was used to confirm the negligible leaching in solution and therefore heterogeneous reaction. These heterogeneous catalyst are stable, showing unobvious activity loss after ten catalytic runs. Additionally, uniform mesopores and the hydrophobic nature of the carbon support may also facilitate the mass transfer of the reactant molecules and enrichment inside pores. Recent

Publications

1. L Djakovitch and F X Felpin (2014) *Chem. Cat. Chem.* 6(8):2175-20187.
2. L L Duan et al. (2016) An efficient reusable mesoporous solid based Pd catalyst for selective C2 arylation of indoles in water. *ACS Catal.* 6(2):1062-1074.

References

1. Chinchilla, R.; Nájera, C. The Sonogashira reaction: A booming methodology in synthetic organic chemistry. *Chem. Rev.* 2007, 107, 874–922. [PubMed]
2. Dieck, H.A.; Heck, F.R. Palladium catalyzed synthesis of aryl, heterocyclic, and vinylic acetylene derivatives. *J. Organomet. Chem.* 1975, 93, 259–263.
3. Cassar, L. Synthesis of aryl- and vinyl-substituted acetylene derivatives by the use of nickel and palladium complexes. *J. Organomet. Chem.* 1975, 93, 253–257.
4. Sonogashira, K.; Tohda, Y.; Hagihara, N. Convenient synthesis of acetylenes. Catalytic substitutions of acetylenic hydrogen with bromo alkenes, iodo arenes, and bromopyridines. *Tetrahedron Lett.* 1975, 16, 4467–4470.
5. Doucet, H.; Hierso, J.-C. Palladium-based catalytic systems for the synthesis of conjugated enynes by Sonogashira reactions and related alkynylations. *Angew. Chem. Int. Ed.* 2007, 46, 834–871. [PubMed]
6. Chinchilla, R.; Nájera, C. Chemicals from Alkynes with Palladium Catalysts. *Chem. Rev.* 2014, 114, 1783–1826. [PubMed][Green Version]
7. Evans, G.; Blanchard, N.; Toumi, M. Copper-mediated coupling reactions and their applications in natural products and designed biomolecules synthesis. *Chem. Rev.* 2008, 108, 3054–3131. [PubMed]

8. Santoro, S.; Kozhushkov, S.I.; Ackermann, L.; Vaccaro, L. Heterogeneous catalytic approaches in C-H activation reactions. *Green Chem.* 2016, 18, 3471–3493.
9. Baeza, A.; Guillena, G.; Ramón, D.J. Magnetite and metal-impregnated magnetite catalysts in organic synthesis: A very old concept with new promising perspectives. *ChemCatChem* 2016, 8, 49–67.
10. Szollosi, G. Asymmetric one-pot reactions using heterogeneous chemical catalysis: Recent steps towards sustainable processes. *Catal. Sci. Technol.* 2018, 8, 389–422.
11. Nasrollahzadeh, M.; Atarod, M.; Alizadeh, M.; Hatamifard, A.; Sajadi, S.M. Recent advances in the application of heterogeneous nanocatalysts for Sonogashira coupling reactions. *Curr. Org. Chem.* 2017, 21, 708–749.